

## COMPARISON OF THE WET HEMATITE AND CORUNDUM (0001) SURFACE STRUCTURES DETERMINED BY SYNCHROTRON X-RAY CTR ANALYSIS

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### RESEARCH OBJECTIVES

The surfaces of crystalline minerals generally differ from the bulk structure due to atomic relaxation, expansion, or rearrangement. These changes can have profound effects on the reactivity of the mineral, especially with regard to toxics sorption, catalytic activity, and dissolution. Although modern thermodynamic calculations and structural simulations are now well developed, these still rest on the fundamental underpinning of the experimental determination of the true surface structure. Here we focus on two isostructural phases that behave quite differently in the environment. Hematite is a primary soil mineral with much greater reactivity than corundum. Though itself not found in soils, the corundum (0001) surface structure is a much-used analog for the alumina layers in clays, which also have relatively low reactivity. The aim is to uncover a structural basis for the differences in reactivity.

### APPROACH

We use crystal truncation rod (CTR) surface x-ray diffraction to probe the atomic positions at the surfaces of highly perfect corundum and hematite (0001) crystals under water solutions. Current work utilizes near-neutral water, but will also examine the effect of pH on surface structure. The technique is based on the fact that the crystal surface termination produces streaks (or "rods") in diffraction space perpendicular to the surface. Though they are of low intensity, equivalent to the scattering of a half-plane of atoms, these rods can be quantitatively measured by synchrotron x-ray diffraction. Small changes in the atomic occupations or positions can have large effects on the rod intensities at different positions in diffraction space, and hence the rod measurements can be refined to reveal the atomic structure of the surface.

### ACCOMPLISHMENTS

Our original CTR analysis of the corundum (0001) surface (Eng et al., 2000) shows considerable relaxations of surface atoms down more than 6 atomic layers. The most important aspect is the shift in the aluminum metal ions near the surface towards the gibbsite (AlOOH) structure. An organized layer of sorbed water

is also present. Finally, the surface is perfectly terminated by oxygen ions and the water layer. In the hematite (0001) surface, the results are similar (see Figure 1), but individual iron ions with surrounding oxygens form islands on the surface. These islands allow for lower-coordination attachment points for reacting species, unlike the smooth corundum surface that presents only fully coordinated (saturated) metal sites. This sort of result may be a general reason for enhanced reactivity at particular metal

oxide mineral surfaces. Analogous work on sorption on the same mineral surfaces using GIXAFS techniques (Waychunas, 2002) supports and confirms our results.

### SIGNIFICANCE OF FINDINGS

Besides the important and fundamental connection of reactivity to structure, the work helps to improve our simulation capability for model-reactive-metal-oxide mineral surfaces. The interatomic potentials used for such simulations—usually molecular dynamics—can be adjusted so that computer results closely approximate the experimental surface structures. Then the simulations can be applied with greater confidence to other mineral-water systems, such as goethite-water.

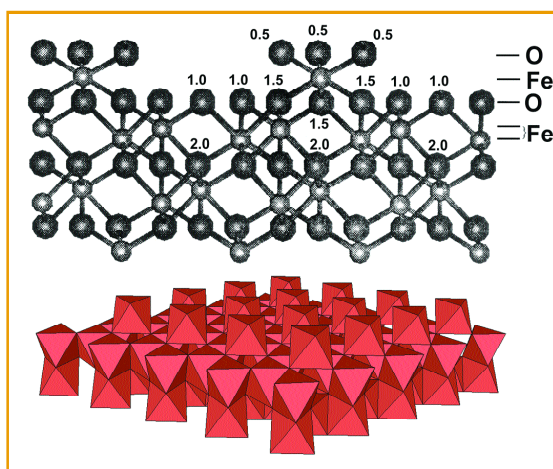


Figure 1. Proposed structure of the hydrated (0001) hematite surface: top: ball and stick structure showing Fe atoms and associated bond valences (inversely related to reactivity); bottom: idealized polyhedral model of the surface. Each octahedron is a FeO<sub>6</sub> unit.

### RELATED PUBLICATIONS

- Eng, P.J., T.P. Trainor, G.E. Brown, G.A. Waychunas, M. Newville, S.R. Sutton, and M.L. Rivers, Structure of the hydrated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0001) surface. *Science*, 288, 1029–1033, 2000.
- Waychunas, G.A., Grazing-incidence X-ray absorption and emission spectroscopy. *Reviews in Mineralogy and Geochemistry*, 49, 267–315, 2002.

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